

Reconstructing Adiabats

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Abstract

We give an explicit method for calculating the equations of state of a thermodynamical substance from the following information: in the calibrated case, the system of isotherms and a *single* adiabat, in the uncalibrated one, the same but with *two* adiabats. For simple examples the entropy function can be computed explicitly from this material but it involves steps (solution of non-linear equations and an integration) which will usually require numerical methods for their implementation.

1 Introduction

The equations of state of a classical Gibbsian thermodynamical system are of the form

$$T = f(p, V), \quad S = g(p, V)$$

where p , V , T and S are the pressure, volume, (absolute) temperature and (absolute) entropy respectively. The isotherms and adiabats are then the level curves of f and g . In [Co] we considered the question of how much information is required to obtain these equations for a given substance. We showed that if one knows T as the function f of p and V and *one* adiabat, i.e., a single level curve of g , then one can recover g . If, on the other hand, one knows only the level curves of T (the isotherms), then *two* adiabats are required.

The reason why this is possible is that f and g are locked into a mutual dependence by the so-called Maxwell relations, one version of which states that the Jacobi determinant

$$\frac{\partial(T, S)}{\partial(p, V)}$$

is identically 1 which means that the mapping from (p, V) -space into (T, S) -space is area-preserving.

In this short article we give a “theory light” version in the form of a step by step method for computing the adiabats from the above information.

We begin with a remark on notation. For our purposes it would be rather confusing to employ the standard thermodynamical variables and we shall use the mathematically neutral letters x and y (which correspond to p and V in Gibbsian thermodynamics) etc. for our variables.

2 Recovering adiabats—the recipe

The general strategy of our method is a standard one in physics—we introduce new coordinates which preserve the essential elements of the situation and reduce the problem to a more tractable one, in this case where the isotherms are parallel lines.

We suppose that we are given the equation of state $T = f(p, V)$ and one adiabat. We use, as mentioned above, x and y as the independent variables. We construct in six steps two coordinate transformations with (X, Y) and (\tilde{X}, \tilde{Y}) for the resulting variables.

Step 1. We introduce new variables

$$X = f(x, y), \quad Y = x.$$

Step 2. We invert the above transformation to get x and y as functions of X and Y .

Step 3. We define a function Ψ as follows:

$$\Psi(X, Y) = - \int \frac{1}{f_y} dY = - \int \frac{dY}{f_y(x(X, Y), y(X, Y))}.$$

Step 4. We then define further new variables

$$\tilde{X} = X, \quad \tilde{Y} = \Psi(X, Y).$$

Again, we invert the transformation to get (x, y) as functions of \tilde{X} and \tilde{Y} .

Step 5. We consider the one given adiabat which we assume is defined implicitly by the equation $g(x, y) = 0$. Then this curve is transformed into the equation $h(\tilde{X}, \tilde{Y}) = 0$ in the (\tilde{X}, \tilde{Y}) -plane where

$$h(\tilde{X}, \tilde{Y}) = g(x(\tilde{X}, \tilde{Y}), y(\tilde{X}, \tilde{Y})).$$

We write the equation of this curve as the graph of a function in the form $\tilde{Y} = f(\tilde{X})$ by solving $h(\tilde{X}, \tilde{Y}) = 0$ for \tilde{Y} . Then the entropy function in the

transformed plane is $\tilde{Y} - f(\tilde{X})$ and so the adiabats in (\tilde{X}, \tilde{Y}) -space are the translates of the given one.

Step 6. The adiabats in (x, y) -space are then the transforms of this family, i.e., the entropy function is $\tilde{Y}(x, y) - f(\tilde{X}(x, y))$ and the adiabats are its level curves.

In order to illustrate this process, we begin with a simple example—the ideal gas where each of the above steps can be carried out explicitly: of course, in this case we know what the result should be but it is interesting to see how the method pulls the familiar logarithmic term in the formula for the entropy out of the hat.

Our starting point is the equation $X = xy$ which corresponds to Charles' law $T = pV$ for the ideal gas (we omit constants). We assume that we have empirical data on *one* adiabat which we model with a generalised parabola $y = x^\alpha$. We now show that this information suffices to reveal the entropy function and so the family of *all* adiabats.

Step 1. The first transformation is $X = xy$, $Y = x$.

Step 2. We solve for x and y to get $x = Y$ and $y = \frac{X}{Y}$.

Step 3. For Ψ we have

$$\Psi(X, Y) = - \int \frac{1}{x} dY = - \int \frac{1}{Y} dY = - \ln Y.$$

Step 4. Putting this together, we have $\tilde{X} = xy$, $\tilde{Y} = - \ln x$.

Step 5. We can invert these equations to get

$$x = e^{-\tilde{Y}}, \quad y = \tilde{X} e^{\tilde{Y}}.$$

Then the equation $y = x^\alpha$ is transformed to the form $\tilde{Y} + \gamma \ln \tilde{X} + \gamma \tilde{Y} = 0$ where $\gamma = -\frac{1}{\alpha}$ and so the adiabat is the graph of the function $\tilde{Y} = -\frac{\gamma}{\gamma-1} \ln \tilde{X}$. Translating this function back into one in x and y gives the familiar entropy function

$$S = \frac{1}{\gamma-1} \ln(xy^\gamma)$$

with the corresponding level curves.

This example was chosen for its familiarity and simplicity which allows us to carry out the necessary computations explicitly and by hand.

In practical situations we can expect to meet difficulties

a) in inverting the transformations from the x and y coordinates to X and Y and then to \tilde{X} and \tilde{Y} —this involves solving pairs of non-linear equations for x and y ;

b) in computing the integral used to define Ψ ;
c) in expressing the transform of the given adiabat in the form of the graph of a function—this, again, involves solving a non-linear equation.
For real gases, some of these processes may have to be computed with the aid of numerical methods.

In order to show the practical difficulties which can arise in real gases, we consider the case where $X = \phi(xy)$ for some calibrating function ϕ . This means that Boyle's law but not Charles' holds.

We find this example particularly interesting since it treats a phenomenon which occurs frequently in practice but which is scarcely dealt with in the textbooks, namely one where we have to recalibrate temperature. This means that the first equation of state has the form $T = \phi(pV)$ for some non-trivial calibration function ϕ .

An example of this phenomenon is one due to Feynman [Fe]—we call it the Feynman gas. Here $t = pV$ and $s = pV^{\gamma(t)}$ for a function γ of one variable (we are using lower case letters t and s to indicate that these are empirical temperature and entropy respectively). This example was introduced by Feynman (see [Fe]) to cope with the fact that, in a real gas, the adiabatic index depends on temperature. This is the first example which we have met in the literature where we genuinely have to recalibrate temperature (i.e., Boyle's law holds only in the weak form that pV is constant for constant temperature). This fact is not considered by Feynman but follows from the analysis in [Co] where it was shown that absolute temperature is then given by the equation $T = \phi(t) = \phi(pV)$ where ϕ is a primitive of $\frac{1}{\gamma - 1}$ (recall that γ is now a function of one variable).

For a discussion of the relevance of such recalibrations, see Chang [Ch]. The recalibrations introduced here provide an at least qualitative explanation of the diagram on p. 78 of this reference, displaying comparative data of Le Duc on spirit thermometers.

We return to our example and compute:

$$\Psi(X, Y) = -\frac{1}{\phi'(\phi^{-1}(X))} \ln Y$$

and hence $\tilde{X} = \phi(xy)$, $\tilde{Y} = -\ln x\phi'(xy)$.

We then have

$$x = \exp\left(-\frac{\tilde{Y}}{\phi'(\phi^{-1}(\tilde{X}))}\right), \quad y = \frac{\phi^{-1}(\tilde{X})}{\exp\left(-\frac{\tilde{Y}}{\phi'(\phi^{-1}(\tilde{X}))}\right)}.$$

Once again, we assume that we have one adiabat given in implicit form $g(x, y) = 0$.

Hence the given adiabat transfers to the form

$$g\left(\exp\left(-\frac{\tilde{Y}}{\phi'(\phi^{-1}(\tilde{X}))}\right), \quad \phi^{-1}(\tilde{X})\exp\left(\frac{\tilde{Y}}{\phi'(\phi^{-1}(\tilde{X}))}\right)\right) = 0.$$

In this case, we will generally not be able to solve this explicitly for \tilde{Y} and so will have to employ numerical methods to complete the analysis.

3 Why does this work?

The background for the above method is the well-known fact (perhaps not as well-known as it should be) that each of the four Maxwell relations in thermodynamics is (individually) equivalent to the Jacobian identity $\frac{\partial(S, T)}{\partial(p, V)} = 1$ (see, for example, [Ri]). This means that the corresponding map from the (p, V) -plane into the (S, T) -plane is area-preserving.

Roughly speaking this says that much of the thermodynamical structure remains intact if we subject the variables to an area-preserving transformation of the coordinates. Our method hinges on the fact that the transformation from the (x, y) coordinates to the (\tilde{X}, \tilde{Y}) does two things:

1. it preserves area (this can be easily checked)
- and
2. it straightens out the isotherms, i.e., transforms them to the family of lines parallel to the \tilde{Y} -axis in the (\tilde{X}, \tilde{Y}) -plane.

Once we have this transformation we can reduce the general case to the latter one which is much simpler. For a more detailed and precise treatment we refer again to [Co].

The particular choice of the second coordinate $Y = x$ probably requires some explanation. What we need is a second family of curves which is transversal to the isotherms. We have chosen the simplest one—the lines parallel to the y -axis. This won't work in all situations but will for most isotherms which arise in thermodynamics. If there is a problem, one can replace this family with the lines parallel to the x -axis (the function Ψ then has to be modified accordingly). At any given point, one of the two will work (at least locally).

We remark that it is a well-known fact of differential geometry that a transformation with the above two properties is always possible—we can straighten out suitable families of curves by means of an area-preserving

transformation. Our contribution has been to display a simple method of constructing it explicitly and to point out its relevance for thermodynamics.

4 The uncalibrated case

Since the uncalibrated case is probably of less practical value, we discuss it only briefly. The situation here is that we are given the family of isotherms but not their calibrations—they are specified as the level curves of a function $f(x, y)$ (e.g., empirical temperature). The function f is only determined up to a recalibration since the family of level curves cannot distinguish between f and a function F of the form $\phi \circ f$ where ϕ is a homeomorphism between intervals of the line. In this case, if we have *two* adiabats we can once more recover the whole family of adiabats and the *correct* calibration of f .

In order to do this, we proceed as above to obtain the variables \tilde{X} and \tilde{Y} which straighten out the isotherms. The two adiabats are then transformed into curves with equations $\tilde{Y} = f_0(\tilde{X})$ and $\tilde{Y} = f_1(\tilde{X})$. We introduce the recalibration $\phi(\tilde{X}) = \int (f_1(\tilde{X}) - f_0(\tilde{X})) d\tilde{X}$ and the level curves of the function

$$\frac{\tilde{Y} - f_0(\tilde{X})}{f_1(\tilde{X}) - f_0(\tilde{X})}$$

are the adiabats in the (\tilde{X}, \tilde{Y}) -plane. Then the recalibrated temperature function is $\phi(f(x, y))$ and the adiabats in the (x, y) -plane are the level curves of the functions

$$\frac{\tilde{Y}(x, y) - f_0(\tilde{X}(x, y))}{f_1(\tilde{X}(x, y)) - f_0(\tilde{X}(x, y))}.$$

We illustrate this again with the example of the ideal gas. We assume that the two adiabats are $xy^\gamma = 1$ and $xy^\gamma = e$ and we have mistakenly calibrated the isotherms not with xy but with x^2y^2 . We will show how the knowledge of the two adiabats shows up the calibration error and displays the correct version.

If we carry out the above scheme than we find that the transformation has the form:

$$\tilde{X} = x^2y^2, \quad \tilde{Y} = \frac{1}{2}xy \ln x,$$

with inverse

$$x = \exp\left(\frac{2\tilde{Y}}{\tilde{X}^{\frac{1}{2}}}\right), \quad y = \tilde{X}^{\frac{1}{2}} \exp\left(\frac{-2\tilde{Y}}{\tilde{X}^{\frac{1}{2}}}\right).$$

A simple computation shows that in this case:

$$f_0(\tilde{X}) = \frac{\frac{\gamma}{2} \ln(\tilde{X})}{(\gamma - 1)\tilde{X}^{\frac{1}{2}}}, \quad f_1(\tilde{X}) = \frac{\frac{\gamma}{2} \ln(\tilde{X}) - 1}{(\gamma - 1)\tilde{X}^{\frac{1}{2}}}.$$

Hence their difference is $\frac{1}{(\gamma - 1)\tilde{X}^{\frac{1}{2}}}$ with primitive the square root function (up to a constant) and this determines the correct calibration of the temperature function.

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